Institution: University College London (UCL)

Unit of Assessment: 8 – Chemistry

Title of case study: Raman spectroscopy benefiting the authentication, conservation, display and handling of historic objects

1. Summary of the impact

The Department of Chemistry at UCL has pioneered the use of Raman spectroscopy (RS) for the identification of pigments in and the *in situ* examination of objects that are of artistic, cultural, or historical importance. Until recently this was a relatively unknown and rarely used technique in heritage science. RS is now used regularly by conservators worldwide and has become an important analysis tool in museums and libraries including the Victoria & Albert Museum, the Indianapolis Museum of Art and the Museum of Fine Arts in Boston. Collaboration between the British Library and UCL was highlighted by the House of Lords Science and Technology Committee, helping to promote further collaboration between universities and museums. The use of RS in heritage science has also benefited manufacturers of RS equipment, and has led to enhanced understanding of the histories and care requirements of a wide range of artefacts.

2. Underpinning research

Using his extensive experience of transition metal chemistry, UCL Department of Chemistry researcher Robin Clark (Ramsay Professor 1989-2008; Emeritus Ramsay Professor 2008-present) realised that RS could be used to investigate artists' materials and their degradation products in a novel way. Therefore, he undertook research to enable the full realisation of the potential of RS in the non-destructive technical examination of art objects. The research carried out at UCL has provided a major contribution to this field since 1993, demonstrating the sensitivity and precision of the technique in identifying pigments and other materials, both rapidly and without ambiguity.

RS is a non-destructive technique, making it ideal for the analysis of organic and inorganic pigments in artworks and artefacts on which destructive or sampling techniques – such as powder X-ray diffraction and scanning electron microscopy – may not be permitted. Furthermore, since each distinct material gives rise to a unique Raman spectrum, the technique can be used to identify unambiguously which pigments are present.

One of the Clark group's important contributions to the emerging field was a 1995 study in which they showed that RS is an ideal technique for distinguishing between lead-based yellow pigments used in antiquity. When previous conventional non-destructive spectroscopic analyses were used, these pigments – the two types of lead tin yellow, Pb_2SnO_4 and $PbSn_{1-x}Si_xO_3$, and the similarly coloured and structured lead antimonate, $Pb_2Sb_2O_7$ – were difficult to identify unambiguously in the presence of other compounds commonly found on artefacts, due to their similar, broad electronic spectra. The Clark group demonstrated that the pigments could, however, be readily distinguished *in situ* using RS by comparing the Raman spectra of laboratory-synthesised lead tin oxides and typical contemporary primer and binding agents with those obtained from medieval paintings and manuscripts [1].

During the early work, Clark identified the lack of reference databases for the analysis of pigments using RS and proceeded to collect the first set of pigment reference spectra at several different excitation wavelengths in 1995. This was immediately popular, and both it and an updated database published in 2001 are still extensively used by Raman scientists all over the world working at the arts-science interface. The 2001 work [2] also introduced Fourier-Transform (FT) Raman as another option for the analysis of organic materials, particularly common binders and varnishes, which either show little response to conventional Raman excitation or fluoresce.

In 2001, the Clark group determined under which conditions of laser wavelength, power and irradiation time PbO_2 and common lead pigments Pb_3O_4, PbO and $2PbCO_3 \cdot Pb(OH)_2$ degrade, and through which pathways [3]. Their results revealed how to correctly identify lead pigments originally used on an artwork, and how to recognise when unwanted degradation is occurring during RS analysis. This work also validated previous studies on the identification of lead pigments by RS, and further confirmed that RS could be used *in situ* on such artefacts without causing degradation, allowing other groups to conduct RS studies on lead pigments with confidence.

Contributions to the field also included many studies conducted jointly with cultural heritage institutions [4, 5, 6]. In collaboration with the British Library (BL), the Lindisfarne Gospels (from AD 715-721) were analysed using RS as, although well studied from a palaeographical standpoint, much less was known about the materials used on the manuscripts and the methods used in their construction. The details regarding the use of pigments in such works were previously identified purely by a visual inspection and had become accepted as fact. As such, important information ascribing to date or point of origin for the greater understanding in an historical context remained undiscovered. The analysis performed on the Lindisfarne Gospels revealed the presence of pigments including calcite $CaCO_3$, indigo $C_{16}H_{10}N_2O_2$, orpiment As_2S_3, vergaut (indigo mixed with orpiment), verdigris (uncertain variant), red lead Pb_3O_4, white lead $2PbCO_3\bullet Pb(OH)_2$ and gold, confirming that most of the pigments that were considered to be there were indeed present [4]. Importantly, however, the blue pigment lazurite $Na_8[Al_6Si_6O_{24}]S_n$ was not found on the manuscript; instead, all the blue colouring in the gospels came from indigo (which was readily available in England at the time). Earlier studies of the gospels had implied that there was a trade route in the 8th century between Afghanistan – the location of the only source of lazurite at the time – and Northumberland; in fact, the UCL work found the earliest use of lazurite on an English manuscript to be more than two centuries later [4]. Interesting studies of astronomical and cartographic Islamic folios held at the Bodleian Library, Oxford, were also made [5]. In a further study, the identification of key pigments on "Young Woman Seated on a Virginal" supported work from the History of Art Department at UCL, by providing persuasive evidence consistent with reattribution of this painting to Vermeer [6]. The research led to the sale of this painting by Sotheby's for £16.2 million.

3. References to the research

[1] Synthesis, structural characterisation and Raman spectroscopy of the inorganic pigments lead tin yellow types I and II and lead antimonate yellow: their identification on medieval paintings and manuscripts, R.J.H. Clark, L. Cridland, B.M. Kariuki, K.D.M. Harris and R. Withnall, *J. Chem. Soc. Dalton Trans.*, 2577-2582 (1995) doi:10/chthzg

[2] Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation, L. Burgio and R.J.H. Clark, *Spectrochim. Acta A*, 57(7), 1491-1521 (2001) doi:10/dfc4n2

[3] Raman spectroscopy as a means for the identification of plattnerite (PbO_2), of lead pigments and of their degradation products, L. Burgio, R.J.H. Clark and S. Firth, *Analyst*, 126, 222-227 (2001) doi:10/c52773

[4] The Lindisfarne Gospels and two other 8th century Anglo-Saxon/Insular manuscripts: pigment identification by Raman microscopy, K.L. Brown and R.J.H. Clark, *J. Raman Spectrosc.*, 35(1), 4-12 (2004) doi:10/d4dmbq

[5] Raman spectroscopic analysis of selected astronomical and cartographic folios from the early 13th century Islamic 'Book of Curiosities of the Sciences and Marvels for the Eyes', T.D. Chaplin, R.J.H. Clark, A. McKay and S. Pugh, *J. Raman Spectrosc.*, 37(8), 865-877 (2006) doi:10/fqz458

[6] Pigment identification by spectroscopic means: evidence consistent with the attribution of the Painting 'Young Woman Seated at a Virginal' to Vermeer, L. Burgio, R.J.H. Clark, L. Sheldon and G.D. Smith, *Anal. Chem.*, 77, 1261-1267 (2005) doi:10/b3vt6j

References [1], [4] and [6] best indicate the quality of the underpinning research.

4. Details of the impact

RS is used extensively and is valued as one of the analysis techniques of choice by heritage scientists. It is a highly specific, non-destructive analytical technique that can be applied *in situ*, and is highly sensitive both to the structure and composition of the sample. Clark's fundamental studies, collaboration activities and continuing work in this field provided a vital contribution to the adoption and widespread use of RS in heritage science and museums. His significant contribution has been recognised by The Royal Society, who awarded him the 2008 Bakerian Lecture for "his pioneering work using the technique of RS as applied to artwork and artefacts". The society added:

"The research is having a profound effect on the art, archaeology and museum worlds; he [Clark] has shown that numerous profound and critical issues which could not previously be addressed can now not only be addressed but resolved. This has influenced major institutions such as the Louvre, the Getty, the Metropolitan of New York and the British Museum (among others) to install Raman microscope systems in recognition of their striking effectiveness as analytical tools." [A] Additionally, his work has been further recognised by a number of eminent scientific and scholarly organisations (American Philosophical Society, the Royal Society of Chemistry, the Fondation de la Maison de la Chimie and the Chemical Heritage Foundation) in the last five years, each of which has acknowledged Clark's contribution to bridging the science world with the humanities and arts, and demonstrating chemistry's role in shaping society [B].

The Indianapolis Museum of Art (IMA) and the Victoria & Albert Museum (V&A) in London have both employed former members of the Clark group. Their expertise in RS, developed whilst at UCL, benefits analysis of art and historic artefacts at the institutions. The IMA established a Conservation Science Laboratory in 2011 and one of the first instruments purchased for the new facility was a Raman spectrometer [C], an instrument that vastly expanded the museum's conservation and analytical capabilities. Prior to this, only optical and polarised light spectroscopy were available, techniques that are not only time consuming to use but are of limited value in pigment identification. Around 50 objects are analysed in the facility per year, and RS analysis is applied to all of them at some point during their study [C]. In 2012, in partnership with Cincinnati Art Museum, a combination of RS and X-ray fluorescence spectroscopy were used to map the location of specific pigments and, following a computer reconstruction, revealed the original appearance of the white flowers in Vincent van Gogh's painting of 1890 *Undergrowth with Two Figures*; this reconstruction is now displayed to the public [C].

In 2009, in collaboration with Clark, five miniatures at the V&A were unambiguously confirmed to be modern forgeries (five 'Spanish Forger' paintings), and the detection of metallic bismuth on an illuminated Bourdichon miniature added to the knowledge of trade routes and pigment availability in medieval Europe [D]. Subsequently, in 2010, having benefited from access to the Raman facilities and collaborating with the team at UCL, the V&A purchased its own Raman spectrometer, a resource that is used on a weekly basis [E]. Having a Raman spectrometer available at the V&A has made it possible to analyse non-destructively and *in situ* museum objects that were, until recently, off-limits due to restrictions to their sampling. Furthermore, where inorganic pigments, minerals and gemstones are concerned, analyses now take a few seconds or minutes to complete, bringing about considerable savings in terms of staff time and increasing productivity. In all, around 150 objects are now studied each year using the technique at the V&A, with analysis results not only enabling dating and authentication of collections, but also informing curators as to whether objects are appropriate for proposed exhibitions and impacting upon their conservation [E]. Utilising their own system in 2012, V&A staff were able to investigate distinct "fingerprints" of pigments for different artists, which led to changes in the attributions of three portrait miniatures: the original Tudor portraits of "Mr and Mrs Croker", which have suffered from troubled attribution histories, were attributed to Nicholas Hilliard or his workshop; and a third portrait miniature (miniature 630-1882) was reattributed from Isaac Oliver to Hilliard or his workshop [F].

UK libraries (Bodleian Library and BL) have also benefited from collaborating with the UCL group and implementing RS analysis. By using RS to ascertain and understand the chemical behaviour of specific pigments, conservators are now able to control the display and storage schedule to reduce degradation of objects, understand and update conservation records, add support to conservation strategies, and also provide instructions to readers about certain items for which there may be a health and safety impact; for example, the requirement to wear gloves where poisonous arsenic-containing pigments are identified (especially in the case of Indian manuscripts). Furthermore, the collaboration between UCL and the BL (1996 to 2008) was highlighted in the House of Lords Science and Technology Committee Science and Heritage report as an example of how academics and curators can work together to develop academic agendas whilst answering both curatorial and conservation questions. This same report concluded that collaboration between university and museum-based scientists is crucial to heritage science. Subsequently, the Science and Heritage Programme (established to take forward the recommendations from these reports) has promoted further collaboration of this nature through research clusters and networking funding, with examples reported in the most recent review (2012) [G].

The pigment database developed by UCL is also valued by researchers and is considered significant to the conservation science field because it was one of the first online reference spectra collections for art materials. The Museum of Fine Arts in Boston (MFA) printed out the set of UCL Raman spectra as a reference when they purchased their Raman spectrometer in 2008, and still regularly consult the printouts today [H]. The images of 67 of the Raman reference spectra generated by UCL, along with links to the UCL Raman Spectroscopic Library website, are included in the Conservation & Art Materials Encyclopedia Online (CAMEO) database that was developed by the MFA – a database that is regularly accessed worldwide. The Schorr Family Associate Research Scientist at the MFA said in May 2013: “in the last year, 80,000 unique visitors provided over 250,000 page views. The hits came from 165 countries. A random check of several pigment pages that include UCL reference spectra gave the following hit results over the past year: berberine (14), lazurite (31), malachite (298), orpiment (93), vermilion (219).” [H]

The UCL research has also had an impact on the sale of Raman spectrometers by Renishaw, a world leader in the manufacture and supply of these instruments. The company’s International Sales Manager and Applications Specialist said: “From a commercial aspect the importance of this field of interest [the use of RS in heritage work] has led to a significant number of sales that one could argue would not have been possible without Professor Clark’s fundamental studies”. Renishaw was the first supplier of a high-end bench Raman microscope and today enjoys a dominant position in the marketplace. It sells instruments worldwide [text removed for publication] [I].

5. Sources to corroborate the impact

[A] Supporting statement from The Royal Society – corroborates the impact of the UCL research on the art, archaeology and museum worlds, and that Clark was awarded the Bakerian Lecture for this contribution. Available on request.

[B] Corroboration of the awards won by Clark 2008-13 can be found online: http://bit.ly/17uSG4h.

[C] A supporting statement from Senior Conservation Scientist at the IMA is available on request – corroborates the impact that RS has made at the IMA in the last 5 years. For further corroboration of the impact on the van Gogh painting work see the Artdaily.org article: http://bit.ly/17qISux.

[D] Information relating to the ‘Spanish Forger’ paintings and the Bourdichon Nativity miniature is available on the V&A website at http://bit.ly/1cpil2r and http://bit.ly/HqQ0vb respectively – corroborates that the paintings are now labelled as forgeries and that RS analysis (along with other techniques) changed knowledge of trade routes and pigment availability in medieval Europe.

[E] The Senior Object Analysis Scientist at the V&A can be contacted to corroborate the application of RS by the V&A and its impact on the museum. Contact details are provided separately.

[F] Comparison of English portrait miniatures using Raman microscopy and other techniques, L. Burgio, A. Cesaratto and A. Derbyshire, *J. Raman Spectrosc.*, 43, 1713-1721 (2012) doi:10/ppv – corroborates the use of RS at the V&A in the attribution of three portrait miniatures to Hilliard.

[G] House of Lords Science and Technology Committee Reports on Science and Heritage available online: http://bit.ly/1adiBtS and http://bit.ly/1itnXpT – corroborates that the BL collaboration was highlighted by the committee and that the earlier report led to the establishment of the Science and Heritage Programme, which has promoted further collaboration of this nature.

[H] Supporting statement from Schorr Family Associate Research Scientist at MFA – corroborates the use of the pigment database at MFA and through the CAMEO database. Available on request.

[I] Supporting statement from the International Sales Manager and Applications Specialist at Renishaw – corroborates the impact that the UCL research has had on sales of Renishaw Raman spectrometers. Available on request.